Organic semiconductors for sprayable solar cells: improving stability and efficiency

Final Report
HR0011-07-1-004
and W911NF-06-1-0347

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Organic Semiconductors for Sprayable Solar Cells: Improving Stability and Efficiency (HR0011-07-1-004)
and
Organic Semiconductors for Sprayable Solar Cells (W911NF-06-1-0347)

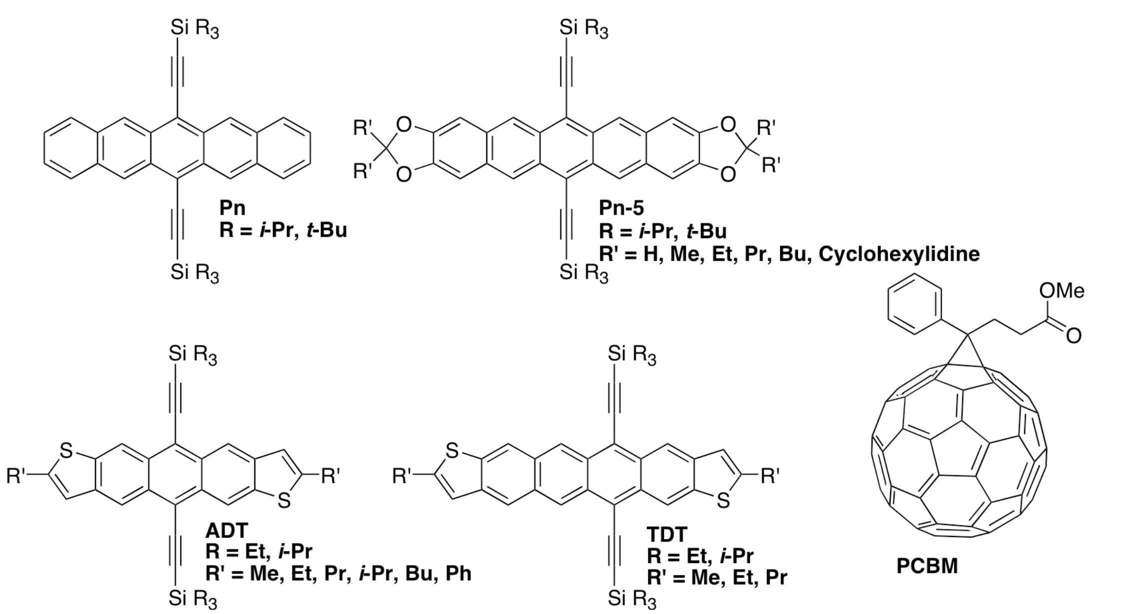
Final report and project summary

Goal of project: We had already demonstrated the feasibility of spray-painted photovoltaics. However, the efficiency of these single-heterojunction devices was remarkably low, they required significant effort to fabricate, and the device lifetimes in air were very short. The aim of this project was thus to simplify fabrication, improve performance and increase device lifetime.

Summary of tasks:

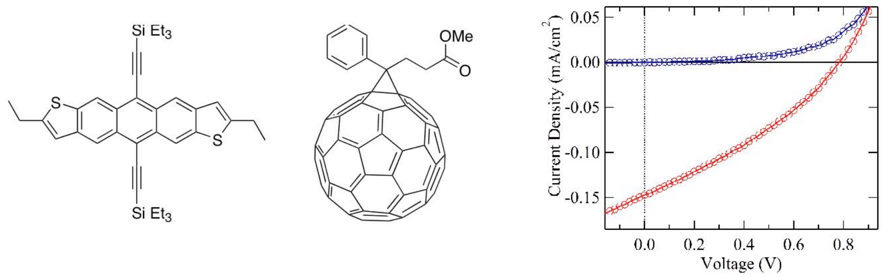
- Screen materials sets – first donors to find best performance, then acceptors
  - What material attributes improve stability? Which improve performance?
    - Feedback yields next generation materials.
- Screen fabrication – find engineering approaches to solve performance issues.
  - Issues with spraying technique of single-heterojunction cells
    - Solvent orthogonality a problem.
  - Issues with film morphology
    - Study on simpler ITO surfaces
  - Issues with poor charge collection from low-conductivity PEDOT/PSS
    - Investigate methods to spray-deposit high performance anode.

Initial materials set:



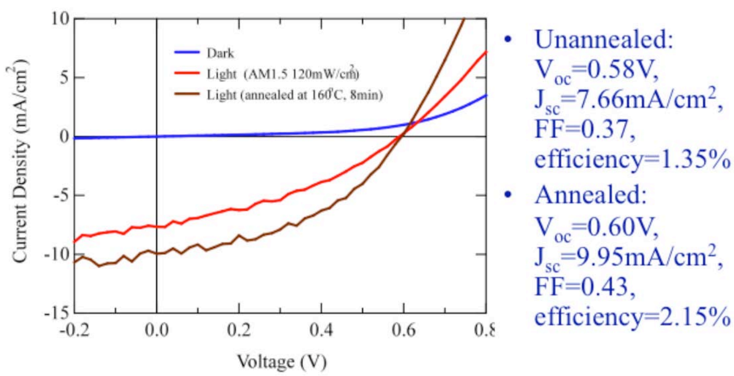
We began by screening the donors shown above (PCBM acceptor) in single-heterojunction devices, as was done in the initial demonstration. The lack of solvent orthogonality between the donors and acceptors led to unacceptable film morphologies, prompting us to decide to adopt a bulk heterojunction approach (where donor and acceptor are mixed before deposition). This decision immediately removed pentacene-based donors from consideration, as these materials react irreversibly with fullerene-based acceptors.

After screening the ADT and TDT donors, we found that ethyl TES ADT (ADT where R = Et, R' = Et) yielded acceptable bulk heterojunction performance. Devices fabricated from spray-painted films of this blend yielded V_{oc} = 0.84 V, I_{sc} = 0.15 mA / cm^2 and an overall efficiency of 0.04% (see below).



Bulk heterojunction solar cell sprayed with Ethyl TES ADT and PCBM

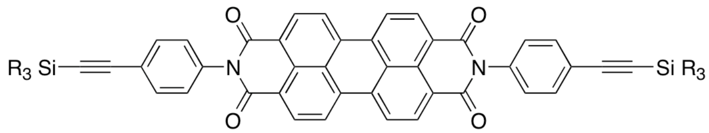
Concurrently, the Cornell group investigated the spray deposition of traditional (poly 3-hexyl thiophene (P3HT) / PCBM) organic solar cell blends. The improved morphology afforded by the polymer led to efficiency of sprayed organic layers as high as 2.15% (see below):



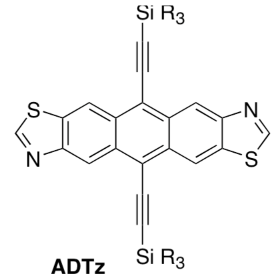
Organic solar cells sprayed from P3HT / PCBM blends

Although performance improved, the cells still suffered from degradation in atmosphere, due to the generation of singlet oxygen by the fullerene (as well as slow oxidation of the fullerene). The Kentucky group thus switched focus to develop new, soluble, air-stable acceptors to match with polythiophene (specifically, P3HT) donors.

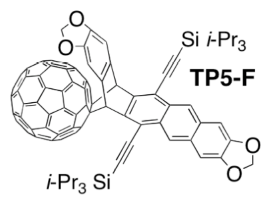
The acceptor systems designed and synthesized by the Kentucky group, then screened by the Cornell group in blends with P3HT, are shown below:



PDI: R = Me, Et, *i*-Pr, *i*-Bu

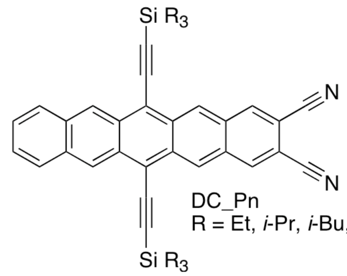


ADTz
R = Me, Et, *i*-Pr, *n*-Pr



TP5-F

E_{red} = -740 mV

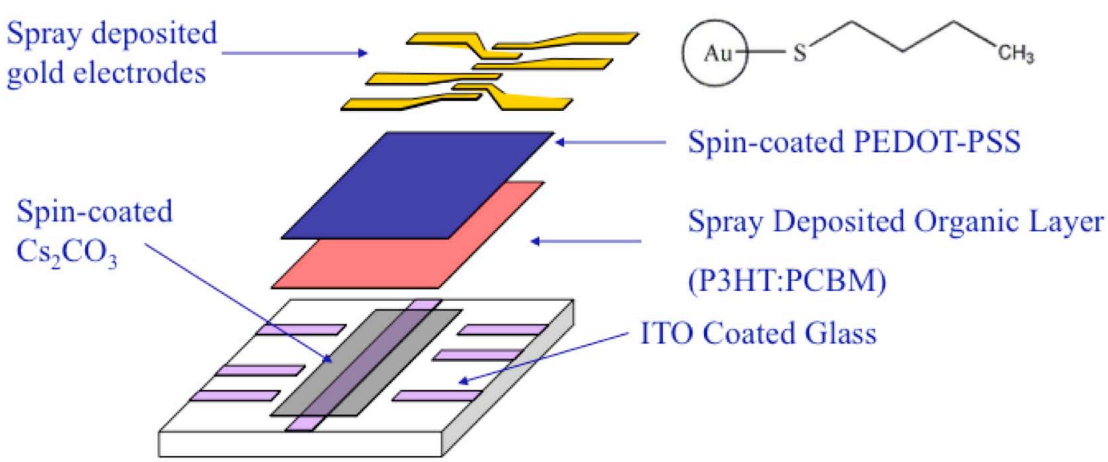


DC_Pn
R = Et, *i*-Pr, *i*-Bu, *n*-Pr, Cyclohexyl, Cyclopentyl

Soluble donors to blend with P3HT

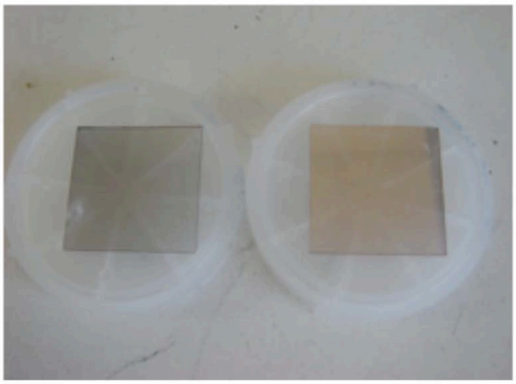
The thiazole derivative (ADTz) was the first screened, and unfortunately did not yield any photovoltaic performance. The fullerene adduct of pentacene and C_{60} was synthesized next – TP5-F yielded an almost 0.8% energy conversion efficiency, but since it proved as unstable as PCBM, this class of materials was dropped. A number of PDIs were tested next. The only derivative to show reasonable photovoltaic performance was PDI (R = Et), which showed a power conversion efficiency of 0.01% (V_{oc} = 0.46 V, I_{sc} = 0.078 mA / cm^2). This can likely be improved by further tuning of the silane substituent (this will continue). The most encouraging acceptor was the dicyano pentacene chromophore (DC_Pn). The derivatives shown above varied in efficiency from 0.001% to 0.5%, with the best being the Cyclopentyl derivative (V_{oc} = 0.6 V, I_{sc} = 1.5 mA / cm^2). Further, the photovoltaic cells fabricated with this material showed significantly higher stability than fullerene-based cells – quantification of this stability is currently underway.

The Cornell group also investigated improving the conductivity of the anode by spray-coating gold nanoparticles on top of the PEDOT-PSS layer. Again, for initial testing the cathode consisted of a simple patterned ITO substrate (see below):

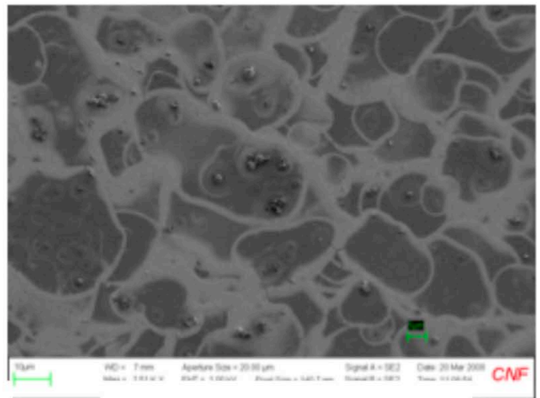


The gold nanoparticles did serve the expected purpose, dramatically increasing the conductivity of the areas of the anode covered by the material. The conductivity was particularly improved upon thermal annealing of the films (190 °C for 1 minute), increasing to as much as 100 ohm / square (see below)

Film of gold nanoparticles has a sheet resistance of about 100-200 Ω / square after annealing (190oC for 1 min), as measured by 4-point probe



Annealed gold film (right) and unannealed film (left)



SEM image of annealed gold film

Project Highlights:

Demonstrated solar cells with reasonable performance from both spray-painted polymer and small-molecule systems.

Developed several classes of viable acceptors for organic photovoltaics (three manuscripts in preparation)

Developed a new acceptor (DC_Pn) that yields cells with improved stability over fullerene-based acceptors, with reasonable performance (manuscript in preparation). Further modifications of molecule and processing conditions should yield performance comparable to that seen in fullerenes.

Developed an approach using Au nanoparticles to improve the conductivity of the conducting polymer anode used in spray-painted solar cells (manuscript in preparation).

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13. ABSTRACT (Maximum 200 words)
This report details the final status of the development of materials and techniques for the fabrication of solar cells by spray-painting. Highlights of the research accomplishments include a demonstration of solar cells with reasonable performance from both spray-painted polymer and small-molecule systems, as well as the exploration of several new classes of viable acceptors for organic photovoltaics (three manuscripts are in preparation on this work). We also developed a new acceptor (DC_Pn) that yields cells with improved stability over fullerene-based acceptors, with reasonable device performance. Further modifications of molecule and processing conditions should yield performance comparable to that seen with fullerene-based acceptors. To improve electrode / organic interfaces, we have concurrently developed an approach using Au nanoparticles to improve the conductivity of the conducting polymer anode used in spray-painted solar cells (manuscript in preparation).

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